

B3

PATENT SPECIFICATION

(11) 1 502 670

1 502 670

- (21) Application N . 45059/75 (22) Filed 30 Oct. 1975
(31) Convention Application No. 49/125 037
(32) Filed 30 Oct. 1974 in
(33) Japan (JP)
(44) Complete Specification published 1 March 1978
(51) INT CL² G03C 1/34
(52) Index at acceptance
G2C 212 25X 27Y 309 326 333 354 362 372 380 C19E2A
C19Y



ERRATA

SPECIFICATION No. 1,502,670

- Page 10, line 127, *after*) *delete* ethyldienyl]-
rhodanine, 5-{{3- *insert* -1-methyl-
ethyldienyl]-3-
Page 13, line 15, *for* azoethiones *read* azole-
thiones
Page 14, line 87, *for* prepared *read* prepara-
tion
Page 16, line 32, *after* further *insert* thermally
THE PATENT OFFICE
24th April, 1978

- 20 photographic materials utilize a composition
containing (a) a silver salt of an organic acid,
(b) a small (catalytic) amount of a light-sen-
sitive silver halide and (c) a reducing agent
for the salt (a). In such a material, the silver
halide remaining undergoes a change in colour
due to standing in the light after development
25 and is not stabilized to light, but this scarcely
matters since only a small amount of silver
halide is used, while a large amount of the
organic silver salt (a) (which is hardly
blackened by light and is white or a pale
30 colour) is used.
This known light-sensitive material is stable
at normal temperature, and in use is imagewise
exposed, and then heated to a temperature of
80° C or higher, preferably 100° C or higher.
35 At this temperature, the organic silver salt (a)
oxidizes the reducing agent (c) to form silver
(images), but only where the catalytic silver
halide (b) was exposed. The exposed areas of
the light-sensitive material are thus blackened
40 while no oxidation-reduction reaction occurs at
the unexposed areas because unexposed silver
halide does not catalyse this reaction. Thus the
unexposed areas remain white and an image
having visible contrast is formed.
45 In such a thermally-developable light-sen-
sitive material, a significant problem remains in
that undesirable darkening in the unexposed or
background areas (called thermal fogging)

and secondary pollution may occur if used
papers supports thereof are recycled.

Other additives used to reduce heat fogging
have impaired the photographic properties of
the material, especially the sensitivity.

Therefore, an object of the present invention
is to provide a thermally-developable light-
sensitive material having low thermal fogging
in the background areas and whereby the
image formed has improved light stability after
thermal development, even after storage at
high temperatures.

According to the invention, a thermally-
development light-sensitive material comprises
a support having therein or in one or more
layers thereon (a) an organic silver salt, (b)
a light-sensitive silver halide or a compound
capable of reacting with said organic silver
salt (a) to form a light-sensitive silver halide,
the component (b) being present in an amount
sufficient to provide silver halide in an amount
which, after exposure to light, catalyses the
reaction of components (a) and (c), and (c)
a reducing agent capable of reducing said
silver salt to silver when heated in the presence
of the silver halide, in or formed from com-
ponent (b) which has been exposed to light,
the material also containing in the support or
in at least one layer on the support, (d) a
neutral complex of palladium with at least
one ligand bonded via a nitrogen, oxygen, sul-

SEE ERRATA SLIP ATTACHED

PATENT SPECIFICATION

(11) 1 502 670

1 502 670

- (21) Application No. 45059/75 (22) Filed 30 Oct 1975
 (31) Convention Application No. 49/125 037
 (32) Filed 30 Oct 1974 in
 (33) Japan (JP)
 (44) Complete Specification published 1 March 1978
 (51) INT CL³ G03C 1/34
 (52) Index at acceptance
 G2C 212 25X 27Y 30⁹ 426 333 354 362 372 380 C19E2A
 C19Y



(54) THERMALLY DEVELOPABLE LIGHT-SENSITIVE MATERIALS

(71) We, FUJI PHOTO FILM CO., LTD., a Japanese Company, of No. 210, Nakamura, Minami/Ashigara-Shi, Kanagawa, Japan, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to an improved type of thermally-developable light-sensitive material.

Silver halide photography has the disadvantage of requiring wet processing steps which are laborious and complex. By contrast, thermally-developable materials can be processed in the dry state.

Known thermally-developable light-sensitive photographic materials utilize a composition containing (a) a silver salt of an organic acid, (b) a small (catalytic) amount of a light-sensitive silver halide and (c) a reducing agent for the salt (a). In such a material, the silver halide remaining undergoes a change in colour due to standing in the light after development and is not stabilized to light, but this scarcely matters since only a small amount of silver halide is used, while a large amount of the organic silver salt (a) (which is hardly blackened by light and is white or a pale colour) is used.

This known light-sensitive material is stable at normal temperature, and in use is imagewise exposed, and then heated to a temperature of 80° C or higher, preferably 100° C or higher. At this temperature, the organic silver salt (a) oxidizes the reducing agent (c) to form silver (images), but only where the catalytic silver halide (b) was exposed. The exposed areas of the light-sensitive material are thus blackened while no oxidation-reduction reaction occurs at the unexposed areas because unexposed silver halide does not catalyse this reaction. Thus the unexposed areas remain white and an image having visible contrast is formed.

In such a thermally-developable light-sensitive material, a significant problem remains in that undesirable darkening in the unexposed or background areas (called thermal fogging)

tends to be produced upon heat development. This fogging relatively reduces the photographic densities in the image areas corresponding to exposed areas.

Moreover, when such light-sensitive materials are stored for a long period of time prior to use, particularly at high temperature (from 30° C to 50° C) and high humidity (relative humidity of 50% or more), thermal fog is also produced.

Methods that have been used in order to eliminate these disadvantages include employing mercuric compounds such as those described in Japanese Patent Publication No. 11113/72; but mercury compounds are highly poisonous and there is the danger that mercury may be evaporated during heat development and secondary pollution may occur if used papers supports thereof are recycled.

Other additives used to reduce heat fogging have impaired the photographic properties of the material, especially the sensitivity.

Therefore, an object of the present invention is to provide a thermally-developable light-sensitive material having low thermal fogging in the background areas and whereby the image formed has improved light stability after thermal development, even after storage at high temperatures.

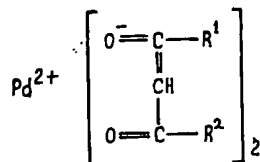
According to the invention, a thermally-developable light-sensitive material comprises a support having therein or in one or more layers thereon (a) an organic silver salt, (b) a light-sensitive silver halide or a compound capable of reacting with said organic silver salt (a) to form a light-sensitive silver halide, the component (b) being present in an amount sufficient to provide silver halide in an amount which, after exposure to light, catalyses the reaction of components (a) and (c), and (c) a reducing agent capable of reducing said silver salt to silver when heated in the presence of the silver halide, in or formed from component (b) which has been exposed to light, the material also containing in the support or in at least one layer on the support, (d) a neutral complex of palladium with at least one ligand bonded via a nitrogen, oxygen, sul-

SEE ERRATA SLIP ATTACHED

phur, phosphorus, arsenic or halogen atom (F, Cl, Br, or I), wherein the ionic charge of the ligand(s) balances the internal charge of the palladium.

- 5 Particularly preferred complexes of palladium are those which are soluble in organic solvents, for example, the palladium complex salt of acetylacetone (referred to merely as "acac" hereinafter).

- 10 Other preferred types of palladium compound which can be used are as follows:
(a) of the general formula:



wherein R^1 and R^2 respectively have the meanings:

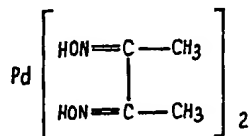
- 15 both are phenyl,
both are methyl,
 R^1 is phenyl and R^2 is methyl, or
 R^1 is trifluoromethyl and R^2 is methyl;
20 (b) of the general formula:



wherein L and X respectively have the meanings:

- 25 L is $\text{C}_6\text{H}_5\text{CH}_2\text{SCH}_2\text{C}_6\text{H}_5$ and X is chlorine;
L is $\text{C}_6\text{H}_5-\text{CN}$ and X is chlorine;
L is $\text{CH}_2=\text{CHCN}$ and X is chlorine;
L is $(\text{C}_6\text{H}_5)_3-\text{P}-$ and X is chlorine;
L is $(\text{C}_2\text{H}_5)_3-\text{P}-$ and X is bromine;
30 L is 1,2-bis($\text{As}-(\text{CH}_3)_2$)-benzene and X is iodine, or
L is bipyridyl and X is chlorine; and

(c) of the general formula:



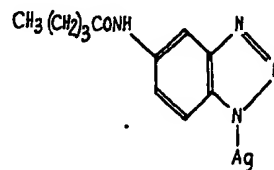
- 35 A suitable amount of the complex of palladium is from about 10^{-6} to 10^{-2} mole, preferably 10^{-6} to 10^{-1} mole, per mole of the organic silver salt [component (a)].

- The organic silver salts employed as component (a) in the invention are colorless, white or slightly colored silver salts which are comparatively stable to light and which react with the reducing agents to form silver images when heated to a temperature of about 80°C or higher, preferably 100°C or higher, in the presence of an exposed silver halide.
45 Examples of organic silver salts include silver salts of organic compounds containing an

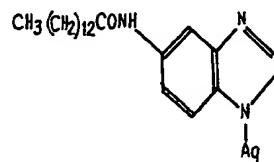
imino group, a mercapto group, a thione group or a carbonyl group. Typical examples of these organic silver salts include (List B): 50

- (1) Silver salts of organic compounds containing an imino group:

Silver benzotriazole, silver nitrobenzotriazole, silver alkyl-substituted benzotriazoles (e.g., silver methylbenzotriazole), silver halogen-substituted benzotriazoles (e.g., silver bromobenzotriazole or silver chlorobenzotriazole), silver carboimide-substituted benzotriazoles, e.g.,



or



silver benzimidazole, silver substituted-benzimidazoles (e.g., silver 5-chlorobenzimidazole or silver 5-nitrobenzimidazole), silver carbazole, silver saccharin, silver phthalazinone, silver substituted-phthalazinone, silver salts of phthalimides, silver pyrrolidone, silver tetrazole and silver imidazole; 65

- (2) Silver salts of organic compounds containing a mercapto group or a thione group: 70

Silver 3-mercapto-4-phenyl-1,2,4-triazole, silver 2-mercaptobenzimidazole, silver 2-mercapto-5-aminothiadiazole, silver 1-phenyl-5-mercaptotetrazole, silver 2-mercaptobenzothiazole, silver salts of the thioglycolic acids as described in Japanese Patent Application (OPI) 28221/73 (e.g., silver 2-(S-ethylenethioglycol-amido)benzthiazole or silver S-alkyl- $(\text{C}_{12}-\text{C}_{22})$ thioglycolates), silver salts of dithiocarboxylic acids (e.g., silver dithioacetate), silver thioamide, silver salts of thiopyridines (e.g., silver 5-carbethoxy-1-methyl-2-phenyl-4-thiopyridine), silver dithiohydroxybenzole, silver mercaptotriazine, silver 2-mercaptobenzoxazole and silver mercaptooxadiazole; 80

- (3) Silver salts of organic compounds containing a carboxylic group: 90

(a) Silver salts of aliphatic carboxylic acids: Silver caprate, silver laurate, silver myristate,

tate, silver palmitate, silver stearate, silver behenate, silver maleate, silver fumarate, silver tartarate, silver furoate, silver linolate, silver leate, silver hydroxystearate, silver adipate, silver sebacate, silver succinate, silver acetate, silver butyrate and silver camphorate;

(b) Silver aromatic carboxylates and other carboxylic acids:

Silver benzoate, silver 3,5 - dihydroxybenzoate, silver *o*-methylbenzoate, silver *m*-methylbenzoate, silver *p*-methylbenzoate, silver 2,4-dichlorobenzoate, silver acetamidobenzoate, silver *p*-phenylbenzoate, silver salts of other substituted benzoic acids, silver gallate, silver tannate, silver phthalate, silver terephthalate, silver salicylate, silver phenylacetate, silver pyromellitate, silver 4' - *n* - octadecyloxydiphenyl - 4 - carboxylate, silver thionecarboxylates as disclosed in U.S. Patent 3,785,830 and silver salts of aliphatic carboxylic acids containing a thioether group as disclosed in U.S. Patent 3,330,663;

(4) Other silver salts:

Silver 4 - hydroxy - 6 - methyl - 1,3,3a,7-tetraazaindene, silver 5 - methyl - 7 - hydroxy-1,2,3,4,6 - pentaazindene, silver tetraazindene as disclosed in British Patent 1,230,642, silver S - 2 - aminophenylthiosulfate as disclosed in U.S. Patent 3,549,379, metal-containing aminoalcohols as disclosed in British Patent No. 1,346,595, and organic acid-metal chelates as disclosed in Belgian Patent 768,411.

An oxidizing agent such as titanium dioxide, zinc oxide or gold carboxylates (e.g., aurous laurate, aurous stearate or aurous behenate) other than silver salts can be employed together with the organic silver salt, if desired.

Various processes are known for preparing such organic silver salts. One of the simplest processes for preparing them is described in U.S. Patent 3,457,075 wherein a solution of an organic silver salt forming agent or a salt thereof in a water-miscible solvent, such as an alcohol or acetone, or water is mixed with an aqueous solution of a water-soluble silver salt such as silver nitrate to prepare an organic silver salt.

Further, it is possible to use the process described in U.S. Patent 3,839,049 wherein a colloidal dispersion of an ammonium salt or an alkali metal salt of an organic silver salt forming agent is mixed with an aqueous solution of a water-soluble silver salt such as silver nitrate. In a similar process, it is possible to use an aqueous solution of a silver complex salt such as a silver amine complex salt or a solution of such a salt in a water-miscible solvent instead of the aqueous solution of the water-soluble silver salt such as silver nitrate.

Another process for preparing organic silver salts is the process described in U.S. Patent 3,458,544. Namely, in this process, organic carboxylic acid silver salts are prepared by

mixing a water difficultly-miscible solution (oily solution) such as a benzene solution of an organic carboxylic acid with an aqueous solution of a silver complex salt. Preferably the water is added to the oily solution to form an emulsion prior to mixing with the aqueous solution of the silver complex salt. This process can be also applied to the preparation of other organic silver salts.

A similar process has been described in Canadian Patent 847,351 wherein the resulting organic silver salts are more stable to heat and light. In this process, a silver salt solution without using an alkali such as an aqueous solution containing only silver nitrate is used instead of the silver complex salt.

Further, a process for preparing organic silver salts is described in West German Patent Application (OLS) 2,402,906. This process is preferred because heat-developable light-sensitive materials containing the resulting organic silver salt do not form as much heat-fog (undesirable fog generated on the unexposed area when the light-sensitive material is heated). Namely, this process comprises mixing an emulsion composed of an aqueous solution of a salt (for example, an alkali metal salt such as a sodium salt, a potassium salt or a lithium salt or an ammonium salt), of a water-soluble organic silver salt forming agent and an oil (for example, benzene, toluene, cyclohexane, pentane, hexane, carboxylic acid esters such as an acetate, phosphoric acid esters, and oils such as castor oil), with a solution of, and preferably an aqueous solution of, a silver salt which is more water-soluble than the organic silver salt, such as silver nitrate) or a silver complex salt to prepare the organic silver salt. In another embodiment of this process, it is possible to prepare the organic silver salt by mixing an aqueous alkali solution (for example, an aqueous solution of sodium hydroxide) with an oil-soluble solution of an organic silver salt forming agent (for example, a toluene solution of the organic silver salt forming agent) and mixing the resulting emulsion with a solution, and preferably an aqueous solution, of a soluble silver salt such as silver nitrate or a silver complex salt such as a silver ammine complex salt.

The oils which can be used for the above-described oily solution include the following compounds:

(1) Phosphoric acid esters:

For example, tricresyl phosphate, tributyl phosphate, and mono-octyl dibutyl phosphate;

(2) Phthalic acid esters:

For example, diethyl phthalate, dibutyl phthalate, dimethyl phthalate, dioctyl phthalate and dimethoxyethyl phthalate;

(3) Carboxylic acid esters:

For example, acetates such as amyl acetate, isopropyl acetate, isoamyl acetate, ethyl acetate, 2-ethylbutyl acetate, butyl acetate and propyl acetate, sebacates such as dioctyl sebacate, di-

butyl sebacate, and diethyl sebacate; succinates such as diethyl succinate; formates such as ethyl formate, pr pyl formate, butyl formate and amyl formate; tartarates such as diethyl tartarate; valerates such as ethyl valerate; butyrates such as methyl butyrate, ethyl butyrate, butyl butyrate and isoamyl butyrate; and adipic acid esters;

(4) Oils such as castor oil, cotton seed oil, linseed oil and tsabaki oil;

(5) Aromatic hydrocarbons such as benzene, toluene and xylene;

(6) Aliphatic hydrocarbons such as pentane, hexane and heptane, and

(7) Cyclic hydrocarbons such as cyclohexane.

Examples of silver complex salts include silver ammine complex salt, silver methylamine complex salt and silver ethylamine complex salt, and preferably alkali-soluble complex salts having a dissociation constant higher than the organic silver salts are suitably used.

Examples of solvents for the silver salts such as silver nitrate include not only water but also polar solvents such as dimethyl sulfoxide, dimethylformamide and acetonitrile.

Further, ultrasonic waves can be employed during the preparation of the organic silver salts as described in West German Patent Application (OLS) 2,401,159. Particularly, emulsification can be easily carried out by applying ultrasonic waves when it is desired to emulsify water and oils. Further, it is possible to use surface active agents for the purpose of controlling the particle size of the organic silver salts during the preparation thereof.

The organic silver salts can also be prepared in the presence of polymers. A specific process has been described in U.S. Patent 3,700,458, which comprises mixing a non-aqueous solution of an organic carboxylic acid with a non-aqueous solution of a heavy metal salt of trifluoroacetate or tetrafluoroborate in the presence of a polymer to produce a heavy metal salt of the organic carboxylic acid such as a silver salt thereof. A process which comprises reacting a colloid dispersion of an organic silver salt forming agent with an aqueous solution of silver nitrate has been described in U.S. Patent 3,839,049. Furthermore, a process for producing an emulsion using similar non-aqueous solutions has been described in U.S. Patent 3,748,143. In addition, it is possible, as described in Japanese Patent Application (OPI) 13224/1974 and West German Patent Application (OLS) 2,322,096, to change the particle form, the particle size and photographic properties such as light stability or sensitivity of the organic silver salts due to the presence of a metal salt or a metal complex such as a mercury or lead compound during the preparation of the organic silver salts.

It has been also confirmed that cobalt,

manganese, nickel, iron, rhodium, iridium, platinum, gold, cadmium, zinc, lithium, copper, thallium, tin, bismuth, antimony, chromium, ruthenium, palladium and osmium in addition to the mercury and lead described above are effective as the metal. In order to use these metal-containing compounds, a mixture or dispersion of a solution of a silver salt forming organic compound and a metal-containing compound can be mixed with an aqueous solution of a soluble silver salt such as silver nitrate or an aqueous solution of a silver complex salt such as a silver ammine complex salt. Further, a solution or dispersion of the metal containing compound can be mixed with an aqueous solution of the silver salt or a silver complex salt and a solution or dispersion of the silver salt forming organic compound. Furthermore, a method comprising mixing a solution or dispersion of the silver salt forming organic compound with a solution or dispersion of a mixture of the silver salt or silver complex salt and the metal-containing compound is also preferred. A preferred amount of the metal-containing compound is from 10^{-4} to 10^{-1} moles per mole of the organic silver salt and from 10^{-3} to 10^{-2} moles per mole of the silver halide.

The particle size of thus-resulting organic silver salts is 0.01 micron to 10 microns along the longer axis and preferably 0.1 micron to about 5 microns.

Examples of light-sensitive silver halides which can be employed as component (b) in the invention include silver chloride, silver bromide, silver iodide, silver chlorobromide, silver chlorobromide, silver chloroiodide, silver iodobromide and a mixture thereof. The light-sensitive silver halide can be in the form of coarse particles or fine particles, but preferably fine particles. A preferred particle size of the silver halide is about 0.001 to 1 micron, more preferably about 0.01 to 0.5 micron, along the longer axis.

The light-sensitive silver halide can be prepared as a photographic emulsion by any of the procedures known in the field of photography, such as a single jet procedure and a double jet procedure. Examples of silver halides used in this invention include these prepared by a Lippmann process, an ammoniacal process and thiocyanate or thioether ripening process. The silver halide used can be unwashed or washed, e.g., with water or an alcohol to remove soluble salts.

The silver halide used in the invention can be chemically sensitized with a chemical sensitizer such as sulfur, selenium, tellurium, gold, platinum, palladium or a reducing agent such as a stannous halide, e.g., as disclosed in U.S. Patents Nos. 1,623,499, 2,399,083 and 3,297,447. The silver halide preferably contains an antifoggant or a stabilizer such as a thiazolium salt, an azaindene, a mercury salt, a urazole, a sulfocatechol, an oxime, a nitron

or a nitroindazole, e.g., as disclosed in U.S. Patents Nos. 2,728,663, 2,839,405, 2,566,263, 2,597,915 and British Patent No. 623,448.

The silver halide emulsion prepared in advance can be mixed with an oxidation-reduction composition comprising an organic silver salt and a reducing agent, as described in U.S. Patent No. 3,152,904. According to this method, however, sufficient contact is not attained between the silver halide and the organic silver salt (e.g., as disclosed in U.S. Patent No. 3,457,075). In order to achieve good contact between the silver halide and the organic silver salt, various techniques can be employed. One effective technique is to mix the materials in the presence of a surface active agent, as described in British Patent No. 1,469,116. According to another method a silver halide is prepared in the presence of a polymer and then mixed with an organic silver salt (for example, as disclosed in U.S. Patent Nos. 3,705,565; 3,713,833; 3,706,564 and 3,761,273; French Patent Nos. 2,107,162 and 2,078,586; and Belgian Patent No. 774,436.

The light-sensitive silver halide employed in the invention can be simultaneously prepared with the preparation of the organic silver salt as disclosed in British Patent No. 1,447,454, by mixing a silver salt (e.g., silver nitrate or a silver complex salt) solution with a solution or dispersion of an organic silver salt-forming compound or a salt thereof and a silver halide forming compound solution, or by mixing a silver halide-forming compound solution and a solution or dispersion of an organic silver salt-forming compound or a salt thereof and a solution of a silver salt such as silver nitrate or a silver complex salt, whereby silver halide is prepared simultaneously with the organic silver salt. Further, the light-sensitive silver halide employed in the invention can be prepared by a partial conversion of the organic silver salt by subjecting a solution or dispersion of the previously prepared organic silver salt to a silver halide forming compound or a sheet material containing an organic silver salt with a silver halide forming compound. The thus-prepared silver halide is in effective contact with the organic silver salt to provide preferred results as disclosed in U.S. Patent 3,457,075.

The light-sensitive silver halide forming components (b) which can be employed in this invention include any compounds capable of forming silver halide on reaction with the organic silver salt. Whether the compounds can be employed as a silver halide forming component can be determined by a routine test. For example, after mixing a compound for forming a silver halide with the organic silver salt, and if necessary heating, the X-ray diffraction pattern obtained by an X-ray diffraction method is examined to determine whether diffraction peaks inherent to silver halide are present.

Examples of silver halide forming components include the following compounds (List B):

(1) Inorganic halides:

Chlorides, bromides and iodides of hydrogen ammonium or a metal; suitable metal atoms include lithium, sodium, potassium, rubidium, cesium, copper, gold, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury, aluminium, gallium, indium, thallium, germanium, tin, lead, antimony, bismuth, chromium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium and platinum.

(2) Halogen-containing metal complexes:

For example, K_2PtCl_6 , K_2PtBr_6 , $HAuCl_4$, $(NH_4)_2IrCl_6$, $(NH_4)_3IrCl_6$, $(NH_4)_2RuCl_6$, $(NH_4)_3RuCl_6$, $(NH_4)_3RhCl_6$ and $(NH_4)_3RhBr_6$.

(3) Onium halides:

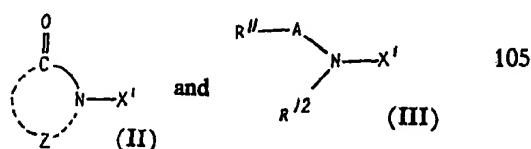
For example, quaternary ammonium halides such as trimethylphenyl ammonium bromide, cetylthylidimethyl ammonium bromide and trimethylbenzyl ammonium bromide, quaternary phosphonium halides such as tetraethyl phosphonium bromide and tertiary sulfonium halides such as trimethyl sulfonium iodide. Further, these onium halides can be used in final coating dispersions for the purpose of decreasing sensitivity or, if desired, decreasing the background density, as described in U.S. Patent 3,679,422.

(4) Halogenated hydrocarbons:

For example, iodoform, bromoform, carbon tetrabromide and 2-bromo-2-methylpropane;

(5) N-halogen compounds:

For example, compounds represented by the following formulae:



wherein X' represents Cl, Br or I; Z represents a group of atoms necessary to form a 5- or 6-membered ring, wherein the 5- or 6-membered ring may be condensed with another ring; A represents a carbonyl group or a sulfonyl group; and R¹¹ and R¹² each represents an alkyl group, an aryl group or an alkoxy group. For example, N-bromosuccinimide, N-bromophthalimide, N-bromoacetamide, N-iodosuccinimide and N-bromophthaladinone are suitable. These compounds have been described in detail in West German Patent Application (OLS) 2,453,131. In addition, N-halo compounds of benzotriazole and substituted benzotriazoles such as the alkyl, nitro, halo, imido or amino substituted benzotriazoles are also effective. Furthermore, N-bromobenzimidazoles are suitable.

(6) Other halogen-containing compounds: For example, triphenylmethyl chloride, triphenylmethyl bromide, 2 - bromobutyric acid, 2 - bromoethanol and dichlorobenzophenone.

5 After the compound (b) which forms the silver halide is added, the coating dispersion can be ripened by allowing the dispersion to stand for a suitable period (for example, 20 minutes to 48 hours) at room temperature (about 20° to 25° C) or at a higher temperature (about 30° to 80° C) to increase the sensitivity and decrease heat fog, or to improve other photographic characteristics, if desired, in the presence of thiosulphate salts, other sulphur-containing compounds, metals such as gold, chromium, tin or lithium, and/or reducing agents.

20 The silver halide forming component (b) can be employed individually or as a mixture. A suitable amount of the silver halide forming component is 0.001 to 0.5 mole, preferably 0.01 to 0.3 mole, per mole of the organic silver salt employed as the component (a). If the amount is more than 0.5 mole, the colour changes which is an undesirable coloration of the background which occurs on allowing the exposed and developed light-sensitive material to stand under normal room illumination. If the amount is less than about 0.001, the sensitivity is reduced.

30 The palladium-containing compound (component (d)) can be added during or prior to formation of the organic silver salt, i.e., in stages prior to the formation of the silver halide (b), or it may be added during the formation of the silver halide as described below, or added after the formation of the silver halide.

40 It is most preferred to add the palladium-containing compound after the formation of the silver halide. In particular, when this is done and the mixture is then allowed to stand at room temperature or higher temperatures (20° C to 80° C) for an adequate time (e.g. 10 minutes to 48 hours), the amount of the palladium-containing compound can be reduced as compared with the cases of a system not subjected to such processing.

50 The reducing agent of component (c) used in the heat developable light-sensitive materials of the present invention is a compound capable of reducing the organic silver salt component (a) when heated in the presence of an exposed silver halide and can be suitably selected depending upon the organic silver salt component (a) with which it is used in combination. Examples of such reducing agents include substituted phenols, substituted or unsubstituted bisphenols, substituted or unsubstituted mono- or bisnaphthols, di- or polyhydroxybenzenes, di- or polyhydroxynaphthalenes, hydroquinone monoethers, ascorbic acid and derivatives thereof, 3 - pyrazolidones, pyrazolin-5-ones, reducing saccharides, aromatic primary amino compounds, reductones, kojic acid,

hinokitiol, hydroxylamines, hydroxytetronic acids, hydroxytetronic acid amides, hydroxamic acids, sulfhydroxamic acids, hydrazides, indan - 1,3 - diones and *p* - oxyphenylglycines. Of these reducing agents, reducing agents which are photolytically decomposed are preferred. Photolytically decomposable reducing agents are described in U.S. Patent 3,827,889. Further, it is possible to use the reducing agents together with compounds which accelerate the photolysis, as described in U.S. Patent 3,756,829. Blocked bisphenol type reducing agents are also used as preferred compounds and have been described in, for example, U.S. Patent 3,589,903 and British Patent No. 1,441,223.

Other examples of the reducing agents which can be used in the present invention are described in U.S. Patents 3,152,904, 3,457,075, 3,531,286, 3,615,533, 3,679,426, 3,672,904, 3,751,252, 3,751,255, 3,782,949, 3,770,448 and 3,773,512, U.S. Patent 3,819,382 and Belgian Patent 786,086.

Examples of suitable reducing agents are as follows:

(1) Substituted phenols:

Aminophenols, for example, 2,4 - diaminophenol, methylaminophenol, *p* - aminophenol, *o* - aminophenol, 2 - methoxy - 4 - aminophenol and 2 - β - hydroxyethyl - 4 - aminophenol; alkyl - substituted phenols, for example, *p* - *t* - butylphenol, *p* - *t* - amylphenol, *p* - cresol, 2,6 - di - *t* - butyl - *p* - cresol, *p* - ethylphenol, *p* - *sec* - butylphenol, 2,3 - dimethylphenol, 3,4 - xyleneol, 2,4 - xyleneol, 2,4 - di - *t* - butylphenol, 2,4,5 - trimethylphenol, *p* - nonylphenol and *p* - octylphenol; other phenols, for example, *p* - acetophenol, *p* - acetoacetyl - 4 - methylphenol, 1,4 - dimethoxyphenol, 2,6 - dimethoxyphenol, chlorothymol, 3,5 - di - *t* - butyl - 4 - hydroxybenzyl - dimethylamine, and sulfonamidophenols, for example, compounds described in U.S. Patent 3,801,321; and novolak resin type reaction products of formaldehyde and phenol derivatives (for example, 4 - methoxyphenol, *m* - cresol, *o* - or *p* - butylphenol, 2,6 - di - *t* - butylphenol and mixtures thereof).

(2) Substituted or unsubstituted bisphenols:

o - bis - Phenols, for example, 1,1 - bis - (2 - hydroxy - 3,5 - dimethylphenyl) - 3,5 - trimethylhexane, bis - (2 - hydroxy - 3 - *t* - butyl - 5 - methylphenyl)methane, bis - (2 - hydroxy - 3,5 - di - *t* - butylphenyl) - methane, bis - (2 - hydroxy - 3 - *t* - butyl - 5 - ethylphenyl)methane, 2,6 - methylene - bis - (2 - hydroxy - 3 - *t* - butyl - 5 - methylphenyl) - 4 - methylphenol, 1,1 - bis - (5 - chloro - 2 - hydroxyphenyl)methane, 2,2' - methylenebis - 4 - methyl - 6 - (1 - methylcyclohexyl)phenol, 1,1 - bis - (2 - hydroxy - 3,5 - dimethylphenyl) - 2 - methylpropane, 1,1,5,5 - tetrakis - (2 - hydroxy - 3,5 - dimethylphenyl) - 2,4 - ethylpentane and 3,3',5,5' - tetramethyl - 6,6' - dihydroxytriphenylmethane; *p* - bis - phenols, for example,

70

75

80

85

90

95

100

105

110

115

120

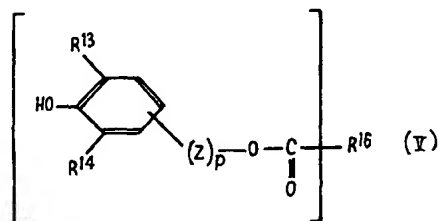
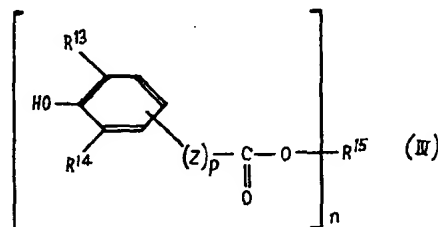
125

130

- bisphenol A, 4,4' - methylene - bis - (3-methyl - 5 - *t* - butylphenol), 4,4' - methylene - bis - (2,6 - di - *t* - heptylidene) - di - (*o* - cresol), 4,4' - ethylidene - bis - (2,6 - di - *tert* - butylphenol), 4,4' - (2 - butylidene) - di - (2,6 - xylenol), 4,4' - (*p* - methylbenzylidene) - di - (*o* - cresol), 4,4' - (*p* - methoxybenzylidene) - bis - (2,6 - di - *tert* - butylphenol), 4,4' - (*p* - nitrobenzylidene) - di - (2,6 - xylenol) and 4,4' - (*p* - hydroxybenzylidene) - di - (*o* - cresol); and others, for example, 3,5 - di - *t* - butyl - 4 - hydroxybenzylidimethylamine, polyphenols such as α,α' - (3,5 - di - *t* - butyl - 4 - hydroxyphenyl)dimethylether, 2,4,6 - tris - (3,5 - di - *t* - butyl - 4 - hydroxybenzyl) - phenol, N,N' - di - (4 - hydroxyphenyl) - urea and tetrakis - [methylene - (3,5 - di - *t* - butyl - 4 - hydroxyhydrocinnamate) - methane, diethylstilbestrol, hexestrol, bis - (3,5 - di - *t* - butyl - 4 - hydroxybenzyl) - ether and 2,6 - bis - (2' - hydroxy - 3' - *t* - butyl - 5' - hydroxybenzyl) - 4 - methylphenol).
- (3) Substituted or unsubstituted mono- or bis-naphthols and di- or polyhydroxy naphthalenes:
bis - β - Naphthols, for example, 2,2' - dihydroxy - 1,1' - binaphthyl, 6,6' - dibromo - 2,2' - dihydroxy - 1,1' - binaphthyl, 6,6' - dinitro - 2,2' - dihydroxy - 1,1' - binaphthyl, bis - (2 - hydroxy - 1 - naphthyl) - methane and 4,4' - dimethoxy - 1,1' - dihydroxy - 2,2' - binaphthyl; naphthols, for example, α - naphthol, β - naphthol, 1 - hydroxy - 4 - aminonaphthalene, 1,5 - dihydroxynaphthalene, 1,3 - dihydroxynaphthalene, 1 - hydroxy - 2 - phenyl - 4 - methoxynaphthalene, 1 - hydroxy - 2 - methyl - 4 - methoxynaphthalene, 1 - hydroxy - 4 - methoxynaphthalene, 1,4 - dihydroxynaphthalene, methylhydroxynaphthalene, sodium 1 - amino - 2 - naphthol - 6 - sulfonate, 1 - naphthylamine - 7 - sulfonic acid and sulfonamidonaphthols.
- (4) Di- or polyhydroxybenzenes and hydroxy - monoethers (e.g., as described in, for example, U.S. Patent 3,801,321):
Hydroquinone; alkyl substituted hydroquinones, for example, methylhydroquinone, *t* - butylhydroquinone, 2,5 - dimethylhydroquinone, 2,6 - dimethylhydroquinone and *t* - octylhydroquinone, etc.; halogen-substituted hydroquinones, for example, chlorohydroquinone, dichlorohydroquinone and bromohydroquinone; alkoxy - substituted hydroquinone, for example, methoxyhydroquinone and ethoxyhydroquinone; other substituted hydroquinones, for example, phenylhydroquinone and hydroquinone monosulfonate; hydroquinone monoethers, for example, *p* - methoxyphenol, *p* - ethoxyphenol, hydroquinone monobenzyl ether, 2 - *t* - butyl - 4 - methoxyphenyl, 2,5 - di - *t* - butyl - 4 - methoxyphenol, hydroquinone mono - *n* - propyl ether and hydroquinone mono - *n* - hexyl ether; and others, for example, catechol, pyrogallol, resorcinol, 1 - chloro - 2,4 - dihydroxybenzene, 3,5 - di - *t* - butyl - 2,6 - dihydroxybenzoic acid, 2,4 - dihydroxybenzoic acid, 2,4 - dihydroxyphenyl sulfide, methyl gallate, and propyl gallate.
- (5) Ascorbic acid and derivatives thereof:
1-Ascorbic acid; isoascorbic acid; ascorbic acid monoesters, for example, ascorbic acid monolaurate, monomyristate, monopalmitate, monostearate and monobehenate; ascorbic acid diesters, for example, ascorbic acid dilaurate, dimyristate, dipalmitate and distearate; and the compounds described in U.S. Patent 3,337,342.
- (6) 3 - Pyrazolines and pyrazolones:
For example, 1 - phenyl - 3 - pyrazolidone, 4 - methyl - 4 - hydroxymethyl - 1 - phenyl - 3 - pyrazolidone, the compounds described in British Patent 930,572, and 1 - (2 - quinolyl) - 3 - methyl - 5 - pyrazolone.
- (7) Reducing saccharides:
For example, glucose and lactose.
- (8) Aromatic primary amino compounds:
Examples of typical compounds include N,N-diethyl - *p* - phenylenediamine - 2 - amino - 5 - diethylaminotoluene, 2 - amino - 5 - (N-ethyl - N - laurylamino) - toluene, 4 - [N-ethyl - N - (β - hydroxyethyl)amino]aniline and 3 - methyl - 4 - amino - N - ethyl - N - (β - hydroxyethyl)aniline, 4 - amino - 3 - methyl - N - ethyl - N - (β - methanesulfoamidoethyl)aniline sesquisulfate monohydrate as described in U.S. Patent 2,193,015, N - (2-amino - 5 - diethylaminophenylethyl)methanesulfoamide sulfate as described in U.S. Patent 2,592,364, N,N - dimethyl - *p* - phenylenediamine hydrochloride and 3 - methyl - 4 - amino - N - ethyl - N - methoxyethylaniline as described in Japanese Patent Application (OPI) 64933/1973, and the inorganic salts thereof. These compounds have been described in L.F.A. Mason, *Photographic Processing Chemistry*, pages 226 to 229, Focal Press, London (1966).
- (9) Hydroxylamines:
For example, N,N - di - (2 - ethoxyethyl)hydroxylamine.
- (10) Reductones:
Anhydro-dihydroaminohexose reductones as described in, for example, U.S. Patent No. 3,679,426 and linear aminoreductones as described in Belgian Patent No. 786,086.
- (11) Hydroxamic acids:
For example, hydroxamic acids as described in U.S. Patents Nos. 3,751,252 and 3,751,255.
- (12) Hydrazides:
For example, hydroxy-substituted aliphatic acid aryl hydrazides as described in U.S. Patent No. 3,782,949.
- (13) Other compounds:
For example, pyrazoline-5-ones as described in U.S. Patent No. 3,770,448, indan-1,3-diones

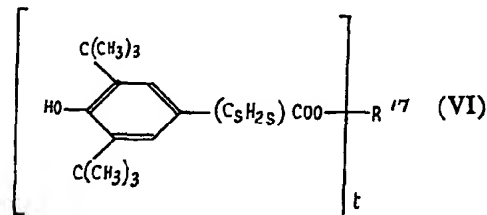
having at least one hydrogen atom at the 2-position thereof as described in U.S. Patent No. 3,773,512; amidoximes as described in U.S. Patent No. 3,794,488, and reducing agents as described in U.S. Patent No. 3,615,533 and U.S. Patent No. 3,819,382, including kojic acid, hinokitiol, hydroxytetronic acid, a hydroxytetronamide, sulphohydroxamic acid and *p*-hydroxyphenylglycine.

Of these reducing agents, the compounds having an alkyl group (e.g., a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group or an amyl group) on at least one position adjacent to the position at which a hydroxyl group is bonded to an aromatic nucleus are preferred because they are stable to light and color change due to exposure to light is small. For example, mono-, bis-, tris or tetrakis phenols having a 2,6-di-*tert*-butyl-phenol group are preferred examples of reducing agents. Typical examples of these compounds are (i) esters of carboxylic acids derived from phenols having a bulky substituent in at least one ortho-position with mono-hydric or poly-hydric alcohols or phenols, and (ii) esters of alcohols derived from phenols having a bulky substituent in at least one ortho-position or phenols having a bulky substituent in at least one ortho-position with mono- or polycarboxylic acids. These esters can be represented by the formulae:



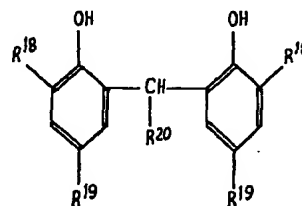
wherein Z is a di-valent group containing up to 30 carbon atoms, R¹³ is an alkyl group having 1 to 20 carbon atoms, R¹⁴ is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, R¹⁵ is an alcohol residue, R¹⁶ is a carboxylic acid residue, *n* and *m* each is a positive integer which is equal to number of alcohol and carboxylic acid residues, respectively, esterified, and *p* is 0 or 1. Specific examples of these compounds includes tetrakis-[methylene - (3,5 - di - *tert* - butyl - 4-hydroxyhydrocinnamate)]methane and octadecyl - 3 - (3',5' - di - *tert* - butyl - 4'-hydroxyphenyl)propionate.

It has been found that, of these esters, those represented by the following general formula (VI) provide an increased image density and desirable black tone when used in combination with phthalazinones, which can be present in the composition according to the invention as a particularly desirable activator toning agent as described hereinafter.



wherein R¹⁷ represents a residue of a saturated acyclic fatty alcohol represented by the formula C_dH_{2d+2+2s}, wherein *d* represents a positive integer of from 1 to 6 and *t* represents a positive integer of from 1 to 4*d*, and *s* represents 1, 2, 3 or 4.

Other preferred reducing agents include, e.g., (blocked) bisphenols having a 2,4-di-*t*-butyl-phenol group or 2,4-di-*t*-amylphenol group. Examples of the bisphenols are compounds shown by the following formula:



In the above formula, R¹⁸ and R¹⁹ represent a *t*-butyl group or a *t*-amyl group, and R²⁰ represents an alkyl group having 1 to 8 carbon atoms.

Further, photodecomposable reducing agents such as ascorbic acid and the derivatives thereof, furoin, benzoin, dihydroxyacetone, glyceraldehyde, rhodizonic acid tetrahydroxyquinone and 4-methoxy-1-naphthol, are preferred. They are decomposed by light even if the light-sensitive materials in which they are present are allowed to stand in the light after development, whereby reduction does not proceed and so no colour change occurs. Furthermore, direct-positive images can be obtained by incorporating a compound which catalyses the destruction of the reducing agent upon imagewise exposure as disclosed in Japanese Patent Publications Nos. 22185/70 and 41865/71.

Two or more reducing agents can be used. Examples of the two or more reducing agents used in combination are disclosed in Japanese Patent Application No. 27242/73 and U.S. Patents Nos. 3,667,958 and 3,751,249. It has

also been confirmed that the development can be accelerated by using the reducing agent in combination with a tin compound, an iron compound, a cobalt compound, or a nickel compound.

A suitable reducing agent used is selected based on the combination of the organic silver salt employed as the component (a) with which the reducing agent is used. For example, a strong reducing agent is suitable for a silver salt such as a silver salt of benzotriazole or silver behenate which is comparatively difficult to reduce, and a weak reducing agent is suitable for a silver salt such as silver caprate or silver laurate which is comparatively easy to reduce. That is, once the organic silver salt is determined, the reducing agent can be selected depending on the organic silver salt. Suitable reducing agents for silver benzotriazole are 1-phenyl-3-pyrazolidones, ascorbic acid, ascorbic acid monoesters and naphthols such as 4-methoxy-1-naphthols. Suitable reducing agents for silver behenate are *o*-bisphenols and hydroquinone. Suitable reducing agents for silver caprate and silver laurate are substituted tetra-kisphenols, *p*-bisphenols such as substituted bisphenol A, and *p*-phenylphenol. The selection of an appropriate reducing agent for the organic silver salt can be facilitated by using two or more reducing agents.

The amount of the reducing agent used in the invention can widely vary depending on the kind of organic silver salt used, the kind of reducing agent used and the other additives present, but the amount of the reducing agent is generally about 0.05 to 5 mols, preferably about 0.1 to 2 mols per mol, of the organic silver salt.

If desired, an auxiliary reducing agent can be used in combination with the reducing agent employed. The amount of the auxiliary reducing agent to be used in the invention can be varied over a wide range, depending on the reducing power of the reducing agents and the reducibility of the organic silver salt used, but a suitable amount of the auxiliary reducing agent generally is from about 10^{-5} to 1 mole, preferably from 10^{-8} to 0.8 mole per mole of the main reducing agent. Examples of effective combinations of reducing agents include a combination of *o*- or *p*-bisphenols and the above described esters selected from esters of mono- or polyhydric phenols or alcohols with carboxylic acids derived from phenols having at least one bulky ortho-substituent, and esters of mono- or poly-carboxylic acids with polyhydric phenols having at least one bulky ortho-substituent or alcohols derived from phenols having at least one bulky ortho-substituent. By use of one of these combinations, a heat developable light-sensitive element having reduced heat-fogging, increased whiteness and improved light stability after development can be obtained.

The combination of two or more mono- or

polyphenolic reducing agents having alkyl groups at both positions adjacent to the position in the aromatic nucleus where the hydroxyl is substituted is effective to prevent light-decoloration.

A compound of tin, iron, cobalt or nickel can be added as a development accelerator.

In forming a black image of silver using the heat developable light-sensitive material of the present invention, a colour toning agent as an additive is preferably incorporated in the material. The colour toning agent is used when it is desired to change the formed image into a deep color image and particularly into a black image. The amount of the color toning agent generally ranges from about 0.0001 mole to about 2 moles, and preferably about 0.0005 mole to about 1 mole, per mol of the organic silver salt. Although the color toning agent which is effective depends upon the organic silver salt and the reducing agent used, in general, heterocyclic organic compounds containing at least two hetero atoms wherein at least one nitrogen atom is present in the ring are used as a color toning agent. These compounds are described in, for example, U.S. Patent 3,080,254. Phthalazine (phthalazinone), phthalic acid anhydride, 2-acetylphthalazinone, 2-phthaloylphthalazinone and substituted phthalazinone derivatives as described in West German Patent Application (OLS) 2,449,252 also can be suitably used in the present invention.

Examples of other effective color toning agents include pyrazolin-5-ones, cyclic imides and quinazolinone, as described in U.S. Patent 3,846,136. For example, phthalimide, *N*-hydroxyphthalimide, *N*-potassium phthalimide and silver phthalimide are typical. Silver phthalazinone is also effective as a color toning agent. Other effective color toning agents are the mercapto compounds described in U.S. Patent 3,832,186 and West German Patent Application (OLS) 2,321,217. In addition, the oxazinediones as described in West German Patent Application (OLS) 2,422,012, the phthalazine diones described in West German Patent Application (OLS) 2,449,252, the uracils described in British Patent No. 1,462,016, the *N*-hydroxynaphthalimides described in U.S. Patent 3,782,941, the substituted phthalimides described in West German Patent Application (OLS) Nos. 2,140,406, 2,141,063 and U.S. Patent 3,844,797, and the phthalazinone derivatives described in West German Patent Application (OLS) No. 2,220,618 can be used too.

Preferably each component used in the present invention is included in a binder so as to provide a homogeneous film on a support. Although preferred binders are generally hydrophobic, hydrophilic binders can also be used. These binders are transparent or semi-transparent. For example, proteins such as gelatin or gelatin derivatives, cellulose deriva-

tives, polysaccharides such as dextran, natural materials such as gum arabic, latex vinyl compounds which increase the dimensional stability of the photographic materials and synthetic polymers described hereinafter can be used. Preferred synthetic polymers are those described in U.S. Patents 3,142,586, 3,193,386, 3,062,674, 3,220,844, 3,287,289 and 3,411,911. Effective polymers include water-insoluble polymers of alkyl acrylates and methacrylates, acrylic acid, sulfoalkyl acrylates or methacrylates, and compounds having a repeating sulfobetaine unit as described in Canadian Patent 774,054. Examples of preferred high molecular weight materials and resins include polyvinyl butyral, polyacrylamide, cellulose acetate butyrate, cellulose acetate propionate, polymethyl methacrylate, polyvinyl pyrrolidone, polystyrene, ethyl cellulose, polyvinyl chloride, chlorinated rubber, polyisobutylene, butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers, vinyl acetate-vinyl chloride-maleic acid-terpolymers, polyvinyl alcohol, polyvinyl acetate, benzyl cellulose, polyvinyl acetate, acetylcellulose, cellulose propionate and cellulose acetate phthalate. Of these polymers, polyvinyl butyral, polyvinyl acetate, ethyl cellulose, polymethyl methacrylate and cellulose acetate butyrate are more preferred. The most preferred material is polyvinyl butyral. If desired, two or more of these materials can be used as a mixture. The ratio by weight of the binder to the organic silver salt of component (a) generally ranges from 10:1 to about 1:10 and preferably 4:1 to 1.4.

The layers containing each component described herein and other layers in the present invention can be applied to many kinds of supports. Examples of supports which can be used in the present invention are synthetic resin films such as cellulose nitrate films, cellulose ester films, polyvinyl acetal films, polyethylene films, polyethylene terephthalate films or polycarbonate films, glass plates, paper and metal plates such as an aluminium plate. Partially acetylated materials can also be used. Further, baryta paper, synthetic resin coated paper and water-resistant paper can be used as well. It is further preferred from the viewpoint of handling that the support is flexible. Art paper, coated paper and clay processed paper are preferred as paper supports. Paper which has been sized with a polysaccharide, etc., is also preferred. The organic silver salt and the silver halide are each used in the amount such that the sum total of silver amount of both coated on the support is about 0.05 g to about 3 g, preferably about 0.1 g to about 2 g, per m² of the support. If the amount coated is below about 0.2 g the image density is low. If the amount coated is above about 3 g, the cost is increased while no additional advantages in photographic properties are achieved.

Certain spectral sensitizing dyes which are

known to be effective for gelatin-silver halide emulsions can be used for the heat developable light-sensitive materials of the present invention in order to further increase the sensitivity. Effective spectral sensitizing dyes include cyanine, merocyanine, complex (trinuclear or tetranuclear) cyanine, holopolar cyanine, styryl, hemicyanine, oxonol and hemioxonol dyes. Of the cyanine dyes, those containing a basic nucleus such as thiazoline, oxazoline, pyrroline, pyridine, oxazole, thiazole, selenazole, or imidazole ring are suitable. Further, such a nucleus can have an alkyl group, an alkylene group, a hydroxyalkyl group, a sulfoalkyl group, a carboxyalkyl group, an aminoalkyl group or an enamine group as a substituent or can form a condensed carbocyclic group or heterocyclic group. The cyanine dyes can be either symmetric or asymmetric. Further, the dyes can have an alkyl group, a phenyl group, an enamine group or a heterocyclic substituent on the methine chain or the polymethine chain thereof. Particularly, cyanine dyes containing a carboxyl group are effective for sensitization. The merocyanine dyes can contain an acid nucleus such as a thiohydantoin nucleus, a rhodanine nucleus, an oxazolidindione nucleus, a thiazolidindione nucleus, a barbituric acid nucleus, a pyrazolone nucleus or a malonitrile nucleus in addition to the above-described basic nucleus. These acid nuclei can be substituted with an alkyl group, an alkylene group, a phenyl group, a carboxyalkyl group, a sulfoalkyl group, a hydroxyalkyl group, an alkoxyalkyl group, an alkylamino group or a heterocyclic nucleus. Particularly, merocyanine dyes having an imino group or a carboxyl group are effective for sensitization. If desired, these dyes can be used as a combination of two or more thereof. Further, they can be used together with ascorbic acid derivatives, azaindenes, cadmium salts, organic sulfonic acids or supersensitizing additives which do not absorb visible light as described in, for example, U.S. Patents 2,933,390 and 2,937,089. Effective sensitizing dyes for the heat-developable light-sensitive materials of the present invention include merocyanine dyes containing a rhodanine nucleus, a thiohydantoin nucleus or a 2-thio-2,4-oxazolidindione nucleus as described in U.S. Patent 3,761,279, for example, 3-p-carboxyphenyl-5-[(β -ethyl-2-(3-benzoxazolyldienyl)ethylidenyl)-rhodanine, 5-[(3- β -carboxyethyl-2-(3-thiazolinyldienyl)ethylidenyl)-3-ethyl]rhodanine, 3-carboxymethyl-5-[(3-methyl-3-thiazolinyldienyl)- α -ethylethylidenyl]rhodanine, 1-carboxymethyl-5-[(3-ethyl-2-(3H)-benzoxazolyldienyl)ethylidenyl]-3-phenyl-2-thiohydantoin, 5-[(ethyl-2-benzoxazolyldienyl)ethylidenyl]-rhodanine, 5-[(3-pyrrolin-1-yl)propyl]rhodanine and 3-ethyl-5-[(3-ethyl-2-(3H)-benzothiazolyldienyl)isopropylidenyl]-2-thio-

70

75

80

85

90

95

100

105

110

115

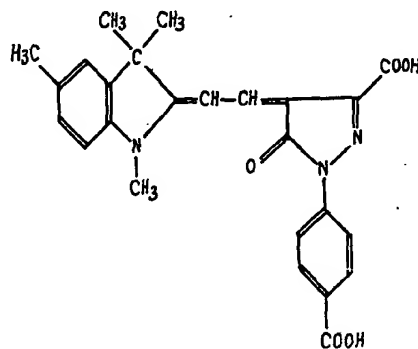
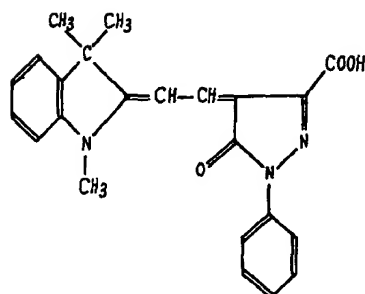
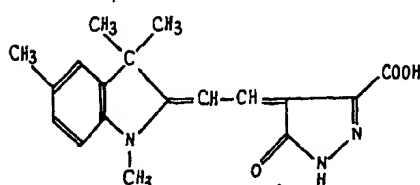
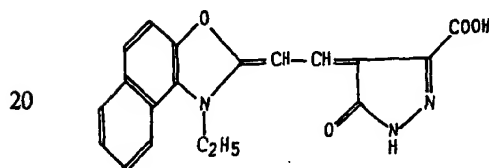
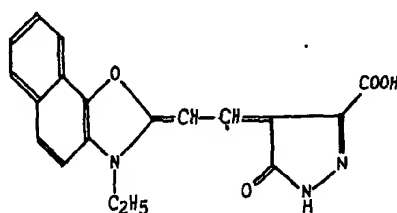
120

125

130

- 2,4 - oxazolidindione. Trinuclear merocyanine dyes as described in U.S. Patent 3,719,495, polynuclear aromatic dyes as described in Belgian Patent 788,695, sensitizing dyes for silver iodide as described in West German Patent Application (OLS) 2,328,868, styrylquinoline dyes as described in West German Patent Application (OLS) 2,363,586, rhodacyanine dyes as described in West German Patent Application (OLS) 2,405,713, acid dyes such as 2',7' - dichlorofluorescein dyes as described in West German Applications (OLS) 2,404,591, 2,401,982, and 2,422,337 and merocyanine dyes as described in British Patents Nos. 1,469,117 and 1,466,201 can also be used.

Examples of effective merocyanine dyes which have pyrazolone nuclei are as follows:



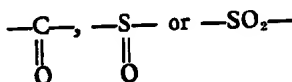
The amount of these dyes generally is from 10^{-4} to 1 mole per mole of the light-sensitive silver halide or the silver halide forming component.

The heat developable light-sensitive materials used in the present invention can have an antistatic layer or an electrically conductive layer. These layers can contain soluble salts such as halides or nitrates, ionic polymers as described in U.S. Patents 2,861,056 and 3,206,312 and insoluble inorganic salts as described in U.S. Patent 3,428,451. Further, the heat-developable light-sensitive materials can have an evaporation-deposited metal layer. If desired, the heat-developable light-sensitive materials of the present invention can contain an antihalation material or an antihalation dye. Preferred examples of such dyes are those dyes which are decolorized upon heat development. For example, the dyes described in U.S. Patents 3,768,019, 3,745,009 and 3,615,432 are preferred. Further, filter dyes or light absorbing materials as described in U.S. Patents 3,253,921, 2,527,583 and 2,956,879 can be incorporated into the heat developable light-sensitive materials of this invention.

If desired, the heat-developable light-sensitive materials of the present invention can contain a matting agent such as starch, titanium dioxide, zinc oxide, silica, polymer beads such as those described in U.S. Patents 2,922,101 and 2,761,245, kaolin or clay. Furthermore, they can contain an optical whitening agent such as the stilbenes, triazines, oxazoles or coumarins as described in, for example, German Patents 972,067 and 1,150,274, French Patent 1,530,244 and U.S. Patents 2,933,390 and 3,406,070. These optical whitening agents can be used as an aqueous solution or as a dispersion.

The heat - developable light - sensitive materials of the present invention can additionally contain a plasticizer and a lubricant. For example, glycerin, diols, polyhydric alcohols as described in U.S. Patent 2,960,404, aliphatic acids or esters as described in U.S. Patents 2,588,765 and 3,121,060

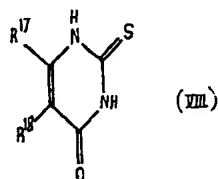
and silicone resins described in, for example, British Patent 955,061 can be used as plasticizers and lubricants. Furthermore, the light-sensitive materials can contain a surface active agent, for example, saponin and alkylaryl sulfonates described in, for example, U.S. Patent 2,600,831, ampholytic compounds described in, for example, U.S. Patent 3,133,816 and addition products of glycidol and alkyl phenols described in, for example, British Patent 1,022,878. Hardenable layers of the heat-developable light-sensitive layers used in the present invention can be hardened by organic or inorganic hardening agents. These hardening agents can be used individually or as a combination of two or more thereof. Preferred hardening agents are aldehydes, blocked aldehydes, ketones, carboxylic acids, carbonic acid derivatives, sulfonic acid esters, sulfonyl halides, vinyl sulfonyl esters, active halogen compounds, epoxy compounds, aziridines, active olefins, isocyanates, carbodiimides and polymeric hardening agents such as dialdehyde starch, etc. Further, many additives can be used for increasing the density of the resulting images. For example, non-aqueous polar organic solvents such as compounds having a



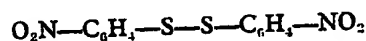
group as described in U.S. Patent 3,667,959, for example, tetrahydrothiophene-1,1-dioxide, 4 - hydroxybutanoic acid lactone and methylsulfinyl methane are effective. Zinc, cadmium and copper acetates as described in U.S. Patent 3,708,304 are also effective. Furthermore, compounds containing water of crystallization as described in U.S. Patent 3,635,719, acid salts of amines and compounds which become alkaline on heating such as metal oxides or hydroxides are effective as the materials for accelerating development. It is possible to use polyalkylene glycols together with mercaptotetrazole in order to improve the sensitivity, contrast and image density as described in U.S. Patent 3,666,477.

Various methods can be utilized in order to further reduce thermal fogging in the heat developable light-sensitive materials of the present invention. One method comprises using mercury compounds, as described in U.S. Patent 3,589,903. Further, it is possible to form direct-positive images using mercury compounds as described in U.S. Patent 3,589,901. Furthermore, the mercury compounds can be used together with color forming couplers in order to form stabilized color images as described in U.S. Patent 3,764,328. A second method for preventing the generation of heat fog is described in West German Patents (OLS) 2,326,865, 2,402,161, 2,364,630, wherein N-halo compounds such

as N - halosuccinimides or N - haloacetamides are used. Other methods for preventing the generation of heat fog are described in U.S. Patent 3,645,739, West German Patent Application (OLS) 2,445,038, and Japanese Patent Applications (OPI) 89,720/1973 and 125016/1074, wherein higher aliphatic acids such as lauric acid, myristic acid, palmitic acid, stearic acid or behenic acid, tetrahalophthalic acid or the anhydride thereof, aryl sulfonic acids such as benzene sulfonic acid or p-toluene sulfonic acid, aryl sulfinic acid or salts thereof such as benzene sulfinic acid or p-toluene sulfinic acid, and lithium salts of higher aliphatic acids such as lithium stearate, are used as acid stabilizing agent. Other effective acid stabilizing agents include salicylic acid, p - hydroxybenzoic acid, tetrabromobenzoic acid, tetrachlorobenzoic acid, p-acetamidobenzoic acid, alkyl substituted benzoic acids such as p-t-butylbenzoic acid, phthalic acid, isophthalic acid, trimellitic acid, pyromellitic acid, diphenic acid, and 5',5'-methylene-bis-salicylic acid. These acid stabilizing agents not only prevent the generation of heat fog but also sometimes have the functions of preventing discoloration when exposed to white light, increasing the image density or improving the shelf life (the property that the photographic properties of the light-sensitive material possessed just after production are maintained after storage). Other compounds which are effective for preventing generation of heat fog are benzotriazole and derivatives thereof, thiouracils, for example, 2-thiouracils represented by the formula (VII):



wherein R¹⁷ represents a hydrogen atom; a hydroxyl group, an alkoxy group, a halogen atom, an unsubstituted or substituted lower alkyl group, a benzyl group, an allyl group, an amino group, a nitro group or a nitroso group, and R¹⁸ represents a hydrogen atom, a hydroxyl group, a halogen atom, an amino group, an acetamido group, an unsubstituted or substituted alkyl group having 1 to 22 carbon atoms, an aryl group, such as a phenyl group, or a substituted aryl group, mercapto compounds such as 1 - phenyl - 5 - mercaptotetrazole, azole thioethers or blocked azolethiones, and peroxides or persulfates or disulfides, e.g. of the formula



as described in British Patent No. 1,460,868. Also, effective prevention of the generation of

13

heat fog or improvement in photographic properties such as sensitization can be achieved if chromium salts, rhodium salts, copper salts, nickel salts, cobalt salts and complex salts of rhodium, iron or cobalt are present during formation or before formation of the silver halide.

In order to prevent discoloration by light of the processed light-sensitive material (the phenomenon in which the unexposed area of the light-sensitive material after processing is discolored gradually by light when exposed to normal room illumination), it is possible to use stabilizer precursors such as azole thioethers or blocked azoethiones as described in U.S. Patent 3,839,049, tetrazolyl thio compounds as described in U.S. Patent 3,700,457 and light-sensitive halogen-containing organic oxidizing agents as described in U.S. Patent 3,707,377.

In addition, it is possible to use light-absorbing dyes as described in British Patent 1,261,102, for, particularly, transmission light-sensitive materials in order to improve the resolving power. Further, it is possible to use leuco dye compounds described in, for example, West German Patent Application (OLS) 2,446,892 in order to improve the shelf life. It is also possible to increase the whiteness by blueing the elements using blue dyes such as Victoria Blue so that the color stain of dyes can be reduced, as described in Japanese Patent Application No. 22135/1974.

Further, it is possible in some cases to stabilize the processed light-sensitive materials to light or heat. Effective methods include the process described in U.S. Patent 3,617,289 which comprises stabilizing the materials using a solution containing mercapto compounds and the method described in West German Patent Application (OLS) 2,443,292 which comprises providing a laminate containing a stabilizing agent.

Further, it is possible to provide, if desired, a top-coating polymer layer on the light-sensitive layer in order to enhance the transparency of the heat developable light-sensitive layer, to increase the image density and to improve the shelf life, as described in West German Patent Application (OLS) 2,323,452. A preferred thickness for the top coating polymer layer ranges from about 1 micron to about 20 microns. Examples of polymers suitable for the top-coat polymer layer include polyvinyl chloride, polyvinyl acetate, vinyl acetate-vinyl chloride copolymers, polystyrene, polymethyl methacrylate, methyl cellulose, ethyl cellulose, cellulose acetate butyrate, cellulose acetate, polyvinylidene chloride, cellulose propionate, cellulose acetate phthalate, polycarbonate, cellulose acetate propionate and polyvinyl pyrrolidone. A top-coat polymer layer containing a material such as kaolin, silica or a polysaccharide such as starch therein, as described in Belgian Patent 798,367 and

Japanese Patent Application (OPI) 46316/1975 provides the heat-developable light-sensitive material with the ability to be written upon with a ball-point pen or a pencil. Further, the top-coat polymer layer can contain a filter dye, an ultraviolet light absorbing agent or an acid stabilizing agent such as a higher aliphatic acid.

The heat developable light-sensitive layers, the top-coat polymer layer, a subbing layer, a back layer and other layers used in the present invention can be coated on a support using various coating methods without the need for a drying step. Examples of such methods are a dip-coating method, an air-knife coating method, a curtain coating method and a hopper coating method. If desired, two or more layers can be coated at the same time using the methods described in U.S. Patent 2,761,791 and British Patent 837,095.

The heat-developable light-sensitive materials of the present invention generally have the characteristic that the photographic properties thereof are easily deteriorated by moisture. Therefore, when the prepared light-sensitive materials are packed for commercial sale, a drying agent, as described in West German Application (OLS) 2,422,040, is generally packed with the materials.

The heat developable light-sensitive materials of the present invention can have a subbing layer between the support and the heat developable light-sensitive layer. Examples of binders which can be used for such a subbing layer include various polymers as described hereinbefore. For example, polyvinyl butyral, polyacrylamide, cellulose acetate butyrate, cellulose acetate propionate, polymethyl methacrylate, polystyrene, polyvinyl pyrrolidone, ethyl cellulose, polyvinyl chloride, chlorinated rubber, polyisobutylene, butadiene-styrene copolymers, vinyl chloride-vinyl acetate copolymers, vinyl acetate-vinyl chloride-maleic acid terpolymers, polyvinyl alcohol, polyvinyl acetate, cellulose acetate, cellulose propionate, cellulose acetate phthalate, gelatin, gelatin derivatives and polysaccharides, can be used. It is possible to improve the photographic properties such as light-discoloration or heat fog, by incorporating aliphatic acids or metal salts thereof in the subbing polymer layer. Further, it is possible to prevent permeation of solvents by incorporating pigments such as clay into the subbing layer. In addition, a matting agent such as silica, kaolin, titanium dioxide or zinc oxide can be added to the subbing layers. Further, a non-electrolytic deposition layer composed of a conductive metal as described in U.S. Patent 3,748,137 can be present. It is also possible to improve the moisture-resistance or to prevent curling in the case of a paper support by providing a hydrophobic polymer layer on the back of the support.

When the desired components are incorporated in a support, e.g. of plastics, glass or metal,

difficulties, of course, arise which may prevent the function(s) of the component(s) from being fully exhibited. However, with a support, e.g., made from paper as a base material, even when some components are incorporated in the support (the paper base material), they show quite the same effect as in the case of incorporating them in a layer or layers coated on the support. Whether the components are incorporated into the support or into the layer(s) coated on the support depends upon various conditions, e.g., the number of production steps desired necessary and advantageous conditions for production. Either embodiment can easily be used, depending on the end-use contemplated.

If desired, a suitable pattern of ink or the like can be printed on the support either on the same side as is coated with a light-sensitive layer or layers or on the side which is not coated with a light-sensitive layer or layers. For example, such would be the case in using this invention for postcards or commuting tickets.

The thus-obtained thermally-developable light-sensitive material is cut to a size suitable for use, and then imagewise exposed. A preheating (at 80° C to 140° C), as mentioned above, can be employed before imagewise exposure.

Suitable light sources for imagewise exposure include a tungsten lamp, a fluorescent copy lamp mainly used for exposure of diazo light-sensitive materials, a mercury lamp, a xenon lamp, a cathode ray tube and a laser.

Photographic images having a continuous tone as well as line images such as drawings can be used as originals. Further, pictures of people and scenes can be directly obtained using a camera. Contact printing, reflection printing, or enlarging printing can be used.

Depending on the sensitivity of the light-sensitive material, in general from 10 lux. sec to 10⁴ lux. sec may be required for the imagewise exposure.

The imagewise exposed light-sensitive material can be developed by simply heating (to 80° C to 180° C, preferably 100° C to 150° C). A suitable duration of heating for development is from 1 second to 60 seconds; the duration depends on the temperature and is usually from 5 to 40 seconds at 120° C, 2 to 20 seconds at 130° C and 1 second to 10 seconds at 140° C.

Many heating means can be utilized for thermally developing the light-sensitive materials of the present invention, for example, the light-sensitive materials can be contacted with a simple heated plate or platen or contacted with a heated drum, or they can be passed through a heated space. Further, they can be heated using high frequency or a laser beam.

The organic silver salt (a), and a reducing agent (c) when thus heated undergo an oxida-

tion-reduction reaction due to the catalytic action of the exposed silver halide (b) present in the vicinity, and finely-divided (black) metallic silver is produced. Thus, the exposed areas of the light-sensitive material are blackened and a difference in contrast arises between the non-exposed areas (background) and exposed areas, to form visible images.

A deodorizer can be included in thermal processing apparatus to remove any odour generated by heating. Also, certain kinds of perfumes can be present in the material so that any such odour is masked.

Methods for specifically preparing exemplary thermally-developable light-sensitive materials according to the present invention are described in detail in the Examples. Briefly, the organic silver salt (a) is prepared by reacting an organic-silver-salt-forming compound with a silver-ion-donating compound, such as silver nitrate, using various methods described already. The prepared is usually carried out at atmospheric pressure, and at a temperature of -15° C to +80° C, suitably 20° C to 60° C. The thus-prepared organic silver salt (a) is rinsed with water or an alcohol and then dispersed in a binder to form an emulsion using a colloid mill, a mixer or a ball mill. The dispersing is usually carried out at room temperature (about 15° C to 25° C). Into the thus-obtained polymer dispersion of the silver salt (a), a silver-halide-forming compound is added to convert a part of the organic silver salt (a) to silver halide (b). A suitable reaction temperature is from room temperature to 80° C. A suitable reaction time is from 1 minute to 48 hours. As was already described, a previously prepared silver halide can be employed, or the silver halide can be prepared at the same time as the organic silver salt. Then the compound (d) and any other additives such as sensitizing dyes, reducing agents (c) and toning agents, are added successively, preferably as solutions. Usually, these additives are added successively into the dispersion with stirring at a temperature of room temperature to 50° C, with a suitable time interval (usually about 5 to 20 minutes) therebetween. Thus a coating composition is obtained after all of the additives are added. The thus-obtained coating composition is coated on a suitable support at 5° C to 50° C at a rate of 3 m/min, to 150 m/min., and dried at 3° C to 100° C. Then, if desired, a top-coat polymer layer can be coated in a similar manner. Further, an undercoat layer can be coated before the other coating solutions are coated, or a backing layer can be coated in a similar manner, or these two layers can be coated at the same time.

The following Examples are given to illustrate the invention.

PREPARATION EXAMPLE 1.

1.9 Grams of sodium hydroxide were dis-

solved in 100 ml of water, which was mixed with a solution of 12 g of lauric acid dissolved in 100 ml of toluene to make an emulsion (at 25° C).

Next, an aqueous solution of 8.5 g of silver nitrate dissolved in 50 ml of water was added. When the mixed solution was allowed to stand for 5 minutes, it separated into a toluene phase containing silver laurate and an aqueous phase. After the aqueous phase was removed, the toluene phase was dispersed in 200 ml of ethanol, and silver laurate was collected by centrifuging. There was thus obtained about 12 g of spindle-shaped silver laurate crystals with a diameter of about 3 microns.

When benzene, pentane, cyclohexane, butyl acetate, isoamyl acetate, butyl alcohol, tricresyl phosphate or dibutyl phthalate was used in place of toluene, silver laurate was produced almost in the same manner.

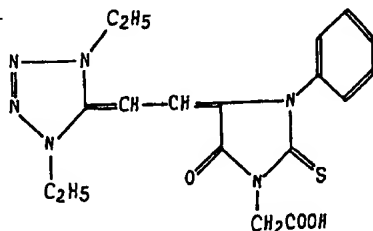
EXAMPLE 1.

6 Grams of the silver laurate produced in the Preparation Example 1 (about 1/50 mole) and 12 g of polyvinyl butyral (or 12 g of ethyl cellulose) were dispersed in 70 g of ethyl alcohol using a mixer to produce a polymer dispersion of the silver salt. The same result was obtained when methanol, propanol or isopropanol was used in place of the ethyl alcohol. Keeping the polymer dispersion of the silver salt at 50° C and stirring using a stirrer, 0.15 g of N-bromosuccinimide (silver halide forming component) was added thereto. Heating was then effected for 90 minutes.

Other N-halogeno compounds such as N-bromoacetamide or N-bromophthalazinone can also be used in place of N-bromosuccinimide.

Thereafter, the temperature was reduced to 30° C and maintained at that temperature. While stirring, the following components were successively added at 5-minute intervals to form a coating composition.

- (a) Pd(acac)₂ (0.1 wt.% acetone solution) 5 ml
(b) sensitizing dye (a merocyanine dye of the following formula):



(0.025 wt.% 2-methoxy ethanol solution) 10 ml

(In place of the above dye, other merocyanine dyes, other cyanine dyes, acid dyes, and the like can be used.)

(c) sodium benzenesulphate dihydrate (stabilizer)

- (0.1 wt.% methanol solution) 5 ml
(d) lauric acid (stabilizer) 55
(3 wt.% ethanol solution) 30 ml
(e) phthalazone (colour toning agent)
(3 wt.% methanol solution) 40 ml
(f) reducing agent 60
2,2 - bis(3,5 - di - methyl - 4 - hydroxy-phenyl) - propne
(20 wt.% acetone solution) 25 ml

The coating composition thus prepared was coated on art paper as a support (other papers such as loaded papers, a photographic base paper, and a base paper for pressure-sensitive papers) and on a polyethylene terephthalate (PET) film as a support at a silver coverage of 0.3 g per m² in the case of the papers and at a silver coverage of 1.5 g per m² in the case of the PET film. In the case of the paper support, a dispersion prepared by dispersing silica into a 10 wt.% ethanol solution of ethyl cellulose was coated on the light-sensitive layer to provide an overcoat polymer layer (containing one part of silica per 10 parts of ethyl cellulose) of a film thickness of about 1.5 microns, and in the case of the film support, a 15 wt.% tetrahydrofuran solution of a copolymer of vinyl chloride and vinyl acetate (weight ratio of 85:15) was overcoated on the light-sensitive layer to provide an overcoat polymer layer of a film thickness of about 3 microns.

The thermally developable light-sensitive materials thus prepared were denoted materials (1) and (1)'. (The symbol with the dash indicates the sample had a PET film support; this convention is used hereinafter).

For comparison, thermally developable light-sensitive materials (2) and (2)' were prepared in the same manner excepting that Pd(acac)₂, the characteristic component of this invention, was omitted.

The thermally developable light-sensitive materials thus prepared were imagewise exposed through an original with gradation to a tungsten light source, the amount of exposure being 10⁴ lux . sec, and then developed by heating at 135° C for 3 seconds.

There was no difference in the fresh photographic properties of the images formed among (1), (1)', (2) and (2)' (such a processing is referred to as "fresh" hereinafter).

Thermally developable light - sensitive materials identical to those above were then kept at 50° C and 50% in the dark for one day and then imagewise exposed and developed in the same manner as in "fresh" processing to obtain a step-wise image (such processing is referred to as "forced ageing" hereinafter). (1) and (1)' showed less thermal fog as compared with (2) and (2)'. The characteristic curves of (1) and (2) are shown in the accompanying drawing.

D-log E characteristic curves can be obtained in which the relative exposure amount (log E) is plotted along the abscissa and the photo-

graphic density (measured by the blackened reflection density as a unit of optical density) is plotted along the ordinate.

	Thermal Fog Density
Fresh (1)	0.05
Fresh (2)	0.05
Forced Ageing (1)	0.06
Forced Ageing (2)	0.38

When the same procedures as above were repeated using a silver salt of myristic acid, palmitic acid, stearic acid or behenic acid in place of silver laurate, the results showed the same trends, i.e., the palladium-containing compound of this invention prevents the occurrence of thermal fog with the passage of time.

EXAMPLE 2.

The same method as in Example 1 was repeated, but component (a) as used in Example 1 was added in an amount 1/10 of that used in Example 1, and then heating was effected at 50 °C for 90 minutes. Thereafter, the temperature was reduced to 30° C and maintained at that point. While stirring, components (b), (c), (d), (e) and (f) as were used in Example 1 were added at 5-minute intervals to prepare a coating composition which was coated on art paper as a support as in Example 1 to prepare thermally developable light-sensitive material (2).

When material (2) was subjected to forced ageing processing, the thermal fog density was 0.05, showing no difference from thermally developable light-sensitive material (1) of Example 1.

A further developable light-sensitive material (3) was prepared in the same manner as light-sensitive material (1) except for adding component (a) in an amount 1/10 of that used in Example 1, and then subjected to forced ageing processing. The thermal fog density was 0.20.

As described above, the amount of the palladium-containing compound can be reduced by varying the addition method.

COMPARATIVE EXAMPLE 1.

The procedure of Example 1 was repeated except for using an aqueous solution of K_2PdCl_4 or K_2PdBr_4 as described in U.S. Patent No. 2,566,263 in an amount equimolar to component (a) of Example 1 instead of component (a) in Example 1.

When the thermally-developable light-sensitive material thus prepared was subjected to fresh processing, thermal fog was high.

In the case of adding 1×10^{-3} mole of K_2PdCl_4 or K_2PdBr_4 , per mole of silver salt, thermal fog was not increased by fresh processing, but thermally developable light-sensitive materials subjected to forced ageing processing showed increased thermal fog and illustrated a thermal fog density of 0.40. That is, when the amount of the palladium-containing compound is reduced to the numerical amount to prevent an increase in thermal fog in fresh processing, the effect of preventing thermal fog with the passage of time is lost. Therefore, K_2PdCl_4 and K_2PdBr_4 are excluded from the palladium-containing compounds of this invention, since the ionic charge of the ligands (the halogen atoms) does not balance the charge of the palladium—the $PdBr_4$ or $PdCl_4$ moiety has a double negative charge.

EXAMPLE 3.

An aqueous solution of 0.8 g of cetyl-ethyl-dimethyl-ammonium bromide dissolved in 100 ml of water was mixed with 100 ml of toluene to form an emulsion. A solution of 0.425 g of silver nitrate dissolved in 10 ml of water was added thereto to produce silver bromide. The silver bromide was present in the emulsified state. There was then added thereto an emulsion prepared by mixing a solution of 12 g of lauric acid dissolved in 100 ml of toluene with a solution of 1.9 g of sodium hydroxide dissolved in 100 ml of water.

Next, a solution of 8.5 g of silver nitrate dissolved in 50 ml of water was added to produce silver laurate. Thus, a mixture in which silver nitrate and silver laurate were in intimate contact with each other was obtained.

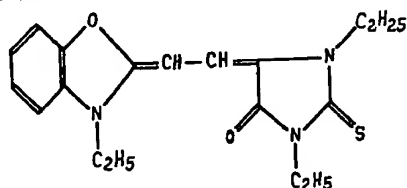
In the above manner, other oils which are relatively immiscible with water can be used in place of toluene, and silver bromide can be replaced with silver bromiodide, silver chlorobromide. Other silver halide forming components can be used in place of cetyl-ethyl-dimethylammonium bromide. In place of silver laurate, other silver salts of aliphatic acids such as silver myristate or silver palmitate can be used, and further, other organic silver salts can easily be used, as will be obvious to those skilled in the art.

The mixture thus formed was collected by centrifuging, and dispersed in 200 g of a solution containing 30 g of polyvinyl butyral (as a binder) in ethanol (other alcohols such as methanol, *n*-propyl alcohol or isopropyl alcohol can be used) by means of a mixer to prepare a polymer dispersion of the silver salts.

The polymer dispersion of the silver salts was kept at 30° C, and the following components successively added thereto at 5-minute intervals to yield a coating composition.

(a) $Pd(acac)_2$
(0.1 wt% acetone solution) 10 ml

- (b) sodium benzenesulfonate dihydrate
(0.1 wt% methanol solution) 20 ml
(c) lauric acid
(3 wt% ethanol solution) 70 ml
(d) dye



- (0.025% methanol solution) 10 ml
(Other merocyanine dyes, cyanine dyes, rhodacyanine dyes, styryl series dyes, acid dyes, and the like can also be used.)

- (e) phthalazone (color toning agent)
(3 wt% methanol solution) 120 ml
(f) reducing agent
tetrakis - [methylene - (3,5 - di - tertiarybutyl - 4 - hydroxyhydro - cinna-
mate)] - methane
(20 wt% acetone solution) 100 ml
(d) Victoria Blue B (blueing agent)
(0.05 wt% methanol solution) 2 ml
(Other blue dyes can also be used)

When high sensitivity is not especially required, the sensitizing dye can be omitted from the above components. Moreover, when an image of a yellowish brown tone is permissible, phthalazone (=phthalazinone) can be omitted.

The coating composition thus prepared was coated on a support base paper (as used for carbonless pressure-sensitive recording paper) at a silver coverage of 0.5 g per m².

An acetone solution of 10 wt% cellulose diacetate containing 1.5wt.% of kaolin was coated on the light-sensitive layer so as to provide a film thickness of 1.5 microns, thus forming an overcoat polymer layer.

When silica was used in the same amount in place of kaolin or art paper was used as the support, equivalent results were obtained.

The thermally developable light-sensitive material thus prepared was referred to as (4). For comparison, a thermally light-sensitive material (5) was prepared which was the same as (4) except that component (a) of this invention, the palladium-containing compound, was omitted.

On comparing the thermal fog densities of thermally developable light-sensitive materials (4) and (5) after fresh processing and forced ageing processing as in Example 1, there was little difference for fresh processing, but for forced ageing processing, the thermally developable light-sensitive material (4) provided less thermal fog than that of (5).

WHAT WE CLAIM IS:—

1. A thermally developable light-sensitive

material comprising a support having thereon or therein in at least one layer

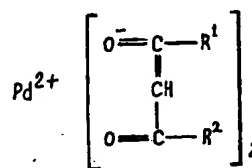
(a) an organic silver salt,
(b) a light-sensitive silver halide or a compound capable of reacting with said organic silver salt (a) to form a light-sensitive silver halide, the component (b) being present in an amount sufficient to provide silver halide in an amount which, after exposure to light, catalyses the reaction of components (a) and (c), and
(c) a reducing agent capable of reducing said silver salt to silver when heated in the presence of the silver halide, in or formed from component (b), which has been exposed to light, the material also containing in the support or in at least one layer on the support,

(d) a neutral complex of palladium with at least one ligand bonded via a nitrogen, oxygen, sulphur, phosphorus, arsenic or halogen atom, wherein the ionic charge of the ligand(s) balances the internal charge of the palladium.

2. A thermally developable material as claimed in Claim 1, wherein said complex of palladium is present in an amount of 10⁻⁸ to 10⁻² mole per mole of the organic silver salt.

3. A thermally developable material as claimed in Claim 1 or 2, wherein said complex of palladium is soluble in an organic solvent.

4. A thermally developable material as claimed in any preceding claim, wherein said complex of palladium is of the general formula:



wherein R¹ and R² respectively have the meanings:

- both are phenyl,
both are methyl,
R¹ is phenyl and R² is methyl, or
R¹ is trifluoromethyl and R² is methyl.

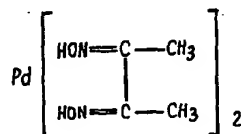
5. A thermally developable material as claimed in any of Claims 1 to 3, wherein said complex of palladium is of the general formula:



wherein L and X respectively have the meanings:

- L is C₆H₅CH₂SCH₂C₆H₅ and X is chlorine;
L is C₆H₅—CN and X is chlorine;
L is CH₂=CHCN and X is chlorine;
L is (C₆H₅)₃—P— and X is chlorine;
L is (C₆H₅)₃—P— and X is bromine;
L is 1,2-bis(As—(CH₃)₂)-benzene and X is iodine, or
L is bipyridyl and X is chlorine.

6. A thermally developable material as claimed in any of Claims 1 to 3, wherein said complex of palladium is of the general formula:



5 7. A thermally developable material as claimed in any of Claims 1 to 3, wherein said complex of palladium is a complex of palladium with acetylacetone.

10 8. A thermally-developable light-sensitive material as claimed in any preceding claim, wherein said organic silver salt (a) is a silver salt of an organic compound containing an imino group, a mercapto group, a thione group or a carboxyl group.

15 9. A thermally-developable light-sensitive material as claimed in any preceding claim, wherein said organic silver salt (a) is a silver carboxylate.

20 10. A thermally-developable light-sensitive material as claimed in Claim 9, wherein said organic silver salt (a) is a silver salt of an aliphatic long-chain fatty acid.

25 11. A thermally-developable light-sensitive material as claimed in any of Claims 1 to 7, wherein the organic silver salt is any of those named herein in List B.

30 12. A thermally-developable light-sensitive material as claimed in any preceding claim, wherein said reducing agent (c) is a substituted phenol, an unsubstituted or substituted bisphenol, an unsubstituted or substituted bisnaphthol, a di- or polyhydroxybenzene, a di- or polyhydroxynaphthalene, a hydroquinone monoether, ascorbic acid or a derivative thereof, a 3 - pyrazolidone, a pyrazolin-5-one, a reducing saccharide, a *p*-phenylenediamine or a derivative thereof, a reductone, kojic acid, hinokitiol, a hydroxylamine, a hydroxytetronic acid, a hydroxytetronamide, a hydroxyoxamic acid, a sulphohydroxamic acid, a hydrazine, an indan-1,3-dione, a *p*-hydroxyphenylglycine, an ester of a carboxylic acid derived from a phenol having a bulky substituent in at least one ortho-position with a monohydric or polyhydric alcohol or phenol, or an ester of an alcohol derived from a phenol having a bulky substituent in at least one ortho-position or a phenol having a bulky substituent in at least one ortho position with a mono- or polycarboxylic acid.

50 13. A thermally-developable light-sensitive material as claimed in any preceding claim, wherein the amount of the reducing agent (c) is from 0.05 to 5 moles per mole of the organic silver salt (a).

14. A thermally-developable light-sensitive material as claimed in Claim 13, wherein the amount of the reducing agent (c) is from 0.1 to 2 moles per mole of the organic silver salt (a).

15. A thermally-developable light-sensitive material as claimed in any preceding claim, containing from 0.2 g to 3 g of silver per square metre in components (a) and (b).

16. A thermally-developable light-sensitive material as claimed in Claim 15, containing from 0.3 g to 2 g of silver per square metre in components (a) and (b).

17. A thermally-developable light-sensitive material as claimed in any preceding Claim, which further contains one or more of a toning agent, a matting agent, an antihalation dye, a fluorescent brightening agent and a spectral sensitizing dye.

18. A thermally-developable light-sensitive material as claimed in any preceding Claim, which further contains a binder.

19. A thermally-developable light-sensitive material as claimed in Claim 18, wherein the weight of the binder is from 1/10 to 10 times that of the organic silver salt (a).

20. A thermally-developable light-sensitive material as claimed in Claim 19, wherein the weight of the binder is from a quarter to quadruple that of the organic silver salt (a).

21. A thermally-developable light-sensitive material as claimed in Claim 1, and substantially as hereinbefore described with reference to any one of thermally developable materials (1), (1)', (2), (3) or (4) in the foregoing Examples.

22. A method of developing a light-sensitive material as claimed in any preceding Claim, which material has been imagewise exposed, comprising heating the material until a visible image is obtained.

23. A method as claimed in Claim 22, wherein the heating step is at a temperature of from 80° to 180° C.

24. A method as claimed in Claim 23, wherein the heating step is at a temperature of from 100° to 150° C.

25. A method as claimed in Claim 22, 23 or 24, wherein the duration of the heating is from 1 to 60 seconds.

26. A material bearing a visible image developed by a method as claimed in any of Claims 22 to 25.

GEE & CO.,
Chartered Patent Agents,
Chancery House, Chancery Lane,
London WC2A 1QU
— and —
39 Epsom Road, Guildford, Surrey,
Agents for the Applicants.

